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International application number: PCT/US05/002490

International filing date: 25 January 2005 (25.01.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/540,673
Filing date: 30 January 2004 (30.01.2004)

Date of receipt at the International Bureau: 03 March 2005 (03.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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APPLICATION NUMBER: 60/540,673

FILING DATE: *January 30, 2004*

RELATED PCT APPLICATION NUMBER: *PCT/US05/02490*



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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53 (b)(2)

13146 U.S. PTO

1546 U.S. PTO
60/540673

Docket Number	81,645	Type a plus sign (+) inside this box →
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TITLE OF THE INVENTION (280 characters max)

SURFACE ACTIVE POLYMERS AS DETERGENTS
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CORRESPONDENCE ADDRESS

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ENCLOSED APPLICATION PARTS (check all that apply)	
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<input checked="" type="checkbox"/> Specification	Number of Pages <u>15</u>	<input type="checkbox"/> Small Entity Statement
<input type="checkbox"/> Drawing(s)	Number of Sheets _____	<input checked="" type="checkbox"/> Other (specify) <u>Postcard</u>

METHOD OF PAYMENT (check one)

<input type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees	PROVISIONAL FILING FEE AMOUNT	\$ 160.00
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge the filing fee to Deposit Account Number: <u>08-3442</u>		

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.
☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

SIGNATURE

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Date

1/30/04

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37,469

☐ Additional inventors are being named on separately numbered sheets attached hereto.

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PROVISIONAL APPLICATION FILING ONLY

Surface Active Polymers as Detergents

Field of the Invention

The present invention provides a new type of surface active polymer which can improve stain removal and modify surfaces.

Description of the Related Art

Polymers are commonly used in cleaning products to chelate hard water ions, control rheology, prevent redeposition, inhibit dye transfer, etc.

Brief Summary of the Invention

The present invention provides surface active polymers which improve soil and stain detergency in formulated liquid detergents. The surface active polymers of the invention not only chelate hard water ions, but also improve stain and soil detergency and modify surfaces to give soil resistance or easier cleaning upon subsequent washes. Careful manipulation of polymer architecture also allows for the possibility of fiber surface modification for soil resistance or easier cleaning upon subsequent washes. The invention is applicable to household laundry applications, but could also be extended to hard surface cleaning.

Detailed Description of the Invention

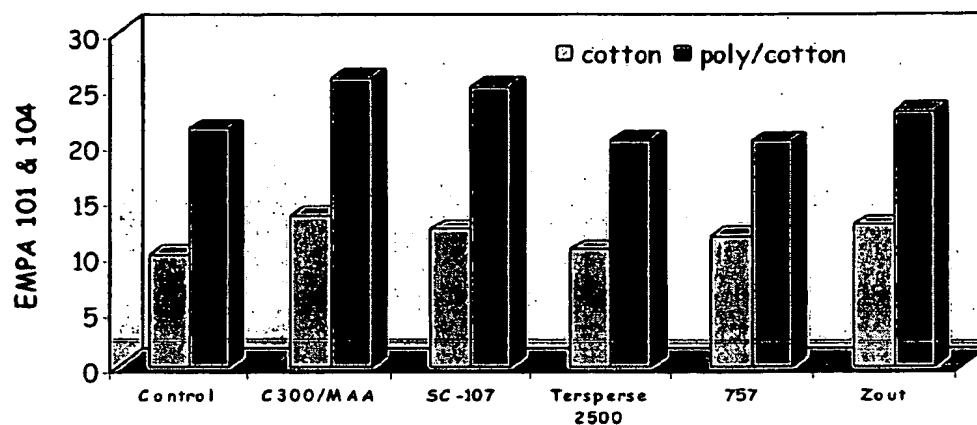
Polymers are currently and commonly used in formulated cleaning products to chelate hard water ions, control rheology, inhibit CaCO_3 crystal growth, prevent redeposition of soil, and inhibit dye transfer. The surface active polymers in the present invention can perform many of the functions of traditional polymers but also improve detergency but modify the surface properties for hydrophobic to hydrophilic and vise versa.

The effect of different polymers on soil and stain removal in a simple laundry pretreatment formulation was determined. Samples were prepared using 8% tridecyl alcohol (TDA) ethoxylate with 8 moles of ethylene oxide. 4 different polymers were evaluated at a level of 1% active polymer. C-300 Acrylate was prepared reacting C-300 detergent product (available from Huntsman LLC Houston, Texas) with maleic anhydride, and copolymerizing the resulting product with methacrylic acid to yield a polymer (molecular weight c.a. 10,000 M_n avg.) with a hydrophilic backbone and hydrophobic grafts. HARTOMER ® SC-107 copolymer product (available from Huntsman LLC Houston, Texas) is a random copolymer prepared using styrene and methacrylic acid. TERSPERSE® 2500 surfactant is product available from Huntsman LLC Houston, Texas. 757 is a random copolymer of styrene and acrylic acid produced by Alco Chemical. The physical properties of each sample are given below. HARTOMER ®SC-107 samples gave good results on oxidizable stains (red wine, tea, fruit juice).

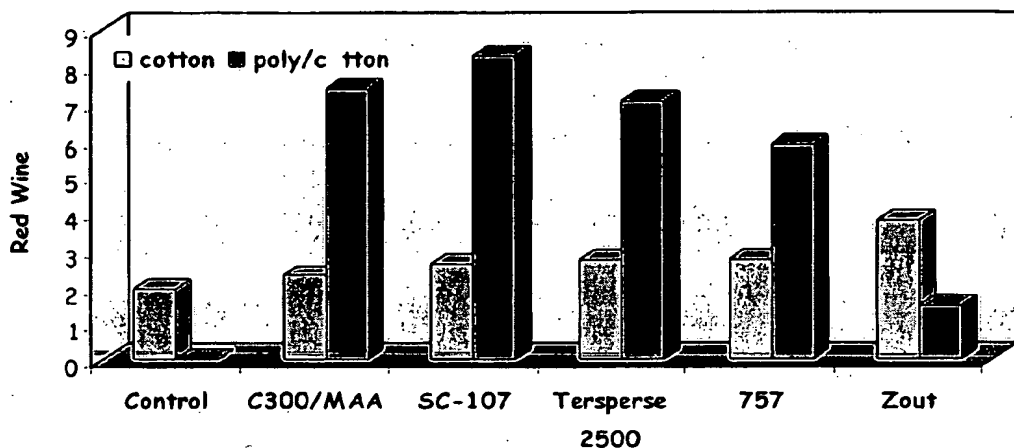
	Control	C300 Acrylate	SC-107	Tersperse 2500	757.00
TDA-8	8	8.00	8.00	8.00	8.00
Polymer	0	4.55	3.57	2.75	2.50
Water	92	87.45	88.43	89.25	89.50
Total	100	100.00	100.00	100.00	100.00
pH	6.58	8.66	8.12	8.76	8.45
viscosity	3	7.00	8.00	5.00	2.00
appearance	C&F	C&F	C&F	C&F	C&F

Each of the solutions was tested as a laundry pretreatment on dust sebum, EMPA 101 & 104 (olive oil), red wine and grass on both cotton and poly/cotton. 1 gm of each solution was applied directly to the soil and allowed to sit 5-10 minutes. Each soil swatch was added to a terge pot at 100°F and 150 ppm water hardness. The swatches were washed for 10 minutes, rinsed, and dried. The reflectance (L of Lab) difference before and after washing was taken as a measure of cleaning performance.

The cleaning performance of the samples on EMPA 101 & 104 (Olive oil based soil) is shown in Fig 1. As a reference, ZOUT® pretreatment (available from the Dial Corporation of Arizona) was included in the evaluation. The higher the bar, the better the cleaning performance. Compared to the control, the C-300 acrylate and HARTOMER® SC-107 gave a noticeable improvement in soil removal on poly/cotton.



The cleaning performance on red wine is shown in Fig 2. The C300 Acrylate and HARTOMER® SC-107 shown excellent stain removal on poly/cotton although all of the polymers tested showed an improvement relative to the control and ZOUT® pre-spotter.

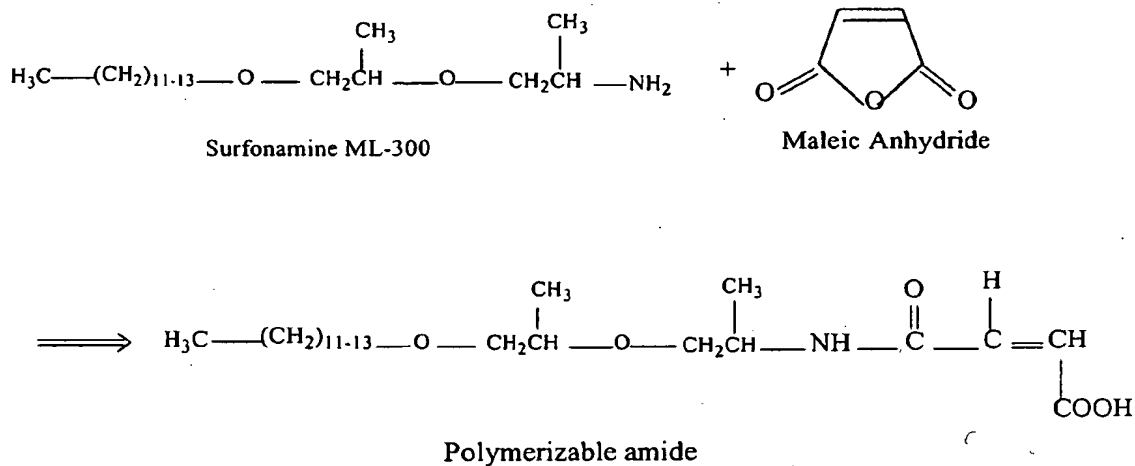


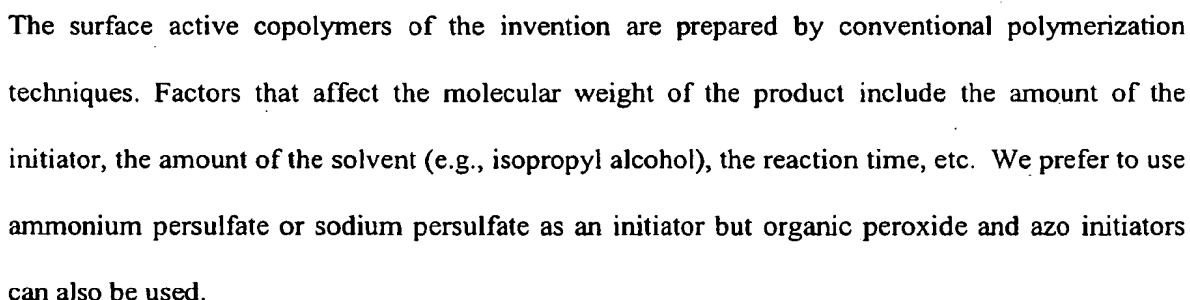
The Surface-Active Water-Soluble Polymers

The anionic surface active water soluble polymers are prepared by copolymerizing polymerizable amides based on polyetheramines with other monomers having vinylic or an allylic moiety to form polymers that exhibit surface activity on par with traditional surfactants. The polymerizable amides are made by reacting the polyetheramines with maleic anhydride.

These novel anionic polymers are soluble in water and exhibit surface active properties like nonionic surfactants such as low critical micelle concentration (CMC) and low surface tension in aqueous solution. The anionic surface active water soluble polymers are prepared by

copolymerizing polymerizable amides based on polyetheramines with other monomers having vinylic or an allylic moiety to form polymers that exhibit surface activity on par with traditional surfactants. The polymerizable amides are made by reacting the polyetheramines with maleic anhydride. These polymerizable amides can be hydrophilic or hydrophobic in nature. For example, a hydrophobic Surfonamine® ML-300 is reacted with maleic anhydride to form the amide which is then copolymerized with hydrophilic monomers such as methacrylic acid, acrylic acid, and acrylamide to form a surface active polymer.





In a round bottom flask, heat 300 g (1.0 mole) of Surfonamine® ML-300 to 60° C (or until liquid). Half of the stoichiometrically-required amount of ground /powdered maleic anhydride ("MA") is slowly added and then stirred until the exotherm kicks in (approx. 10-15 minutes). Then the remainder of the MA powder is slowly added keeping the temperature below 90°C. After addition, the contents of the flask are held at 80°–90°C for at least one hour and then acid numbers are ran (mg KOH/mole) in dry acetone and dry isopropanol. The acid number is checked every 30 minutes until subsequent readings are stable to an acid number variance of less

than about 3 typically taking about 2 hours total time. The expected acid value is in the range of about 138-148, and the difference in acid numbers should be 20-30. If necessary, more MA is added so as to put the acid number (acetone) 20-30 higher than the acid value (isopropanol).

Example 2 - Preparation of ML-300 amide (example 1)/methacrylic acid copolymer (40% ML-300 amide: 60% Methacrylic acid by weight)

A 3-necked 1 L flask is fitted with a mechanical stirrer, heating mantle, thermometer, reflux condenser, addition inlet, and provision for maintaining an inert atmosphere within the reaction vessel, such as a nitrogen inlet. The flask is charged with 142 grams of isopropanol and 104 grams of water. Heating is commenced under stirring and slow nitrogen sweep until a gentle reflux is achieved, at about 80°C. A first stream comprising 74 grams of a 10% aqueous sodium persulfate solution was slowly added to the refluxing contents of the flask simultaneously with a second stream comprising a liquid mixture of 38 grams of ML-300 amide monomer (Example 1) and 57 grams of methacrylic acid, over the course of about 2 hours. Subsequently, an additional 15 grams of 10% sodium persulfate was added and the temperature maintained at reflux for 1 hour to ensure complete reaction. To prepare a water-soluble salt of a copolymer, namely the ammonium salt, the flask was set up for distillation by affixing a head and condenser. The flask is heated until the azeotrope of isopropanol and water begins to distill and then 143 grams of 28% ammonium hydroxide aqueous solution is slowly added to the flask during the distillation at a rate which is approximately equal to the rate at which the azeotrope is being distilled. When the temperature reaches 98-101° C, the flask is allowed to cool to 50°C and 128 grams of water is added to adjust a total solids content to about 22 %. Figure 1 shows the surface tension curve

for the above copolymer in water. As can be seen, the polymer behaves like a surfactant and exhibits surface tension values of 30 dyne/cm at 1000 ppm and 29 dyne/cm at 5000 ppm.

Alkylamide methacrylic acid copolymer Graft Copolymer

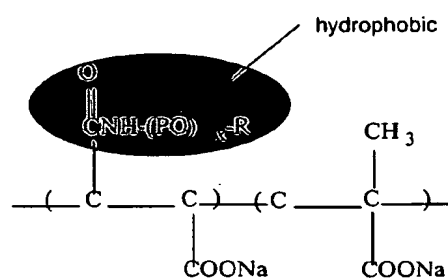
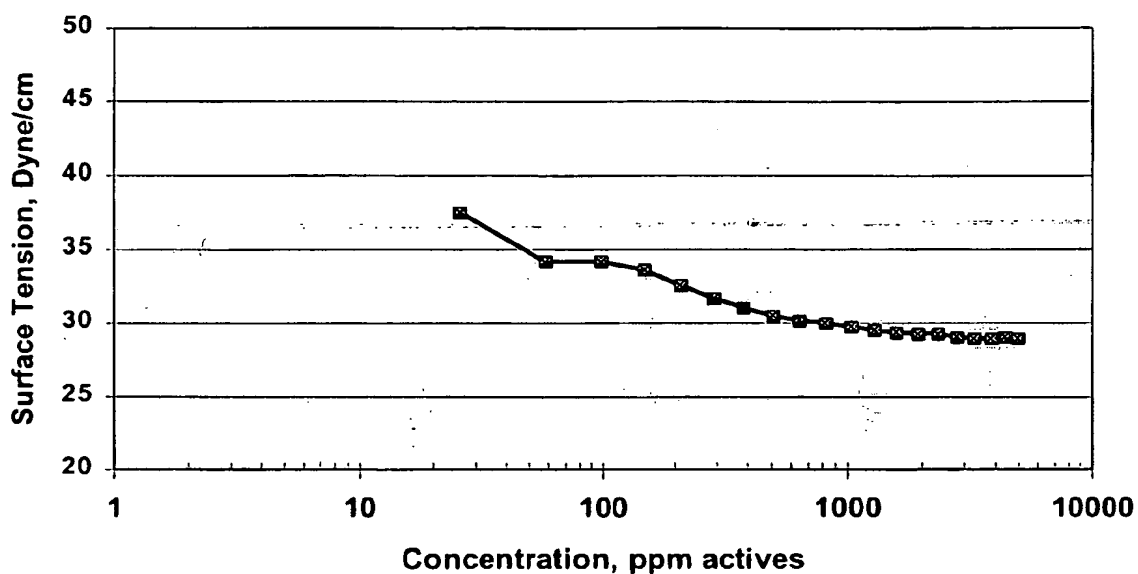


Figure 1

Surface Tension of Surfonamine ML-300 Amide / Methacrylic Acid Copolymer (40:60 by weight) in Water

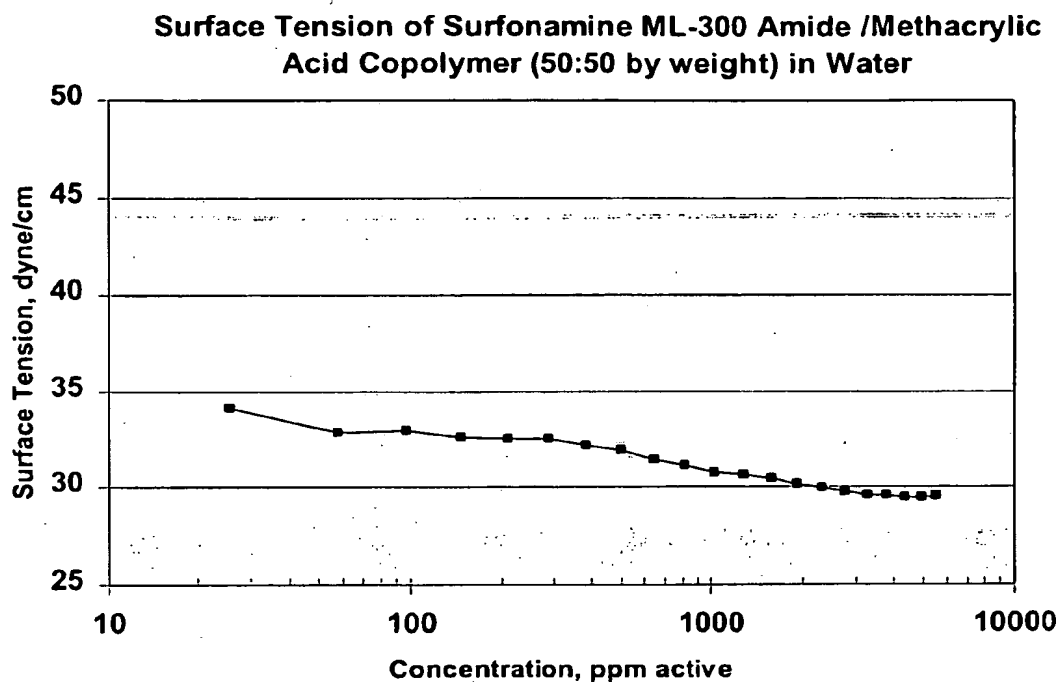


Example 3 - Preparation of ML-300 amide (example 1)/methacrylic acid copolymer (50% ML-300 amide: 50% Methacrylic acid by weight)

By the same procedure described in Example 2, 51 grams ML-300 amide and 51 grams methacrylic acid are copolymerized in isopropanol (151 grams) and water (110 grams) with 78 grams of 10% sodium persulfate aqueous solution. The polymer is neutralized with 107 grams triethanol amine (TEA) and about 136 grams of water is added at the end to obtain 44 % solids. The surface tension curve for this copolymer is shown in Figure 2. It produces lower surface tension values at low concentrations than the copolymer in Example 1. This can be attributed to

a higher content of hydrophobic monomer, 50% vs. 40% by weight, in the copolymer. Again, the copolymer is quite surface active as reflected by low surface tension.

Figure 2



Example 4 - Preparation of ML-300 amide (example 1)/acrylamide copolymer (50% ML-300 amide: 50% acrylamide by weight)

By the same procedure described in Example 2, 58 grams ML-300 amide and 58 grams methacrylic acid are copolymerized in isopropanol (173 grams) and water (127 grams) with 90 grams of 10% sodium persulfate aqueous solution. The polymer is neutralized with 22 grams triethanol amine (TEA) and about 156 grams of water is added at the end to obtain 31 % solids. Figure 3 shows the surface tension of this copolymer in water. This copolymer shows a distinct

critical micelle concentration (CMC) at a very low concentration, 23 ppm and exhibits a minimum surface tension of 30 dyne/cm.

Alkylamide acrylamide copolymer Graft Copolymer

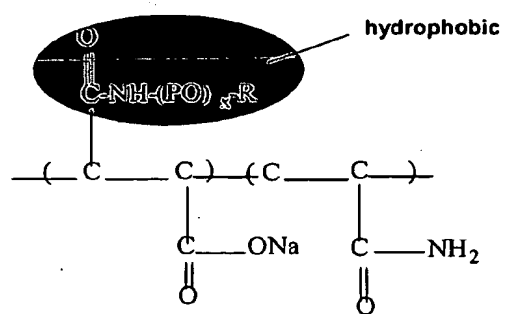
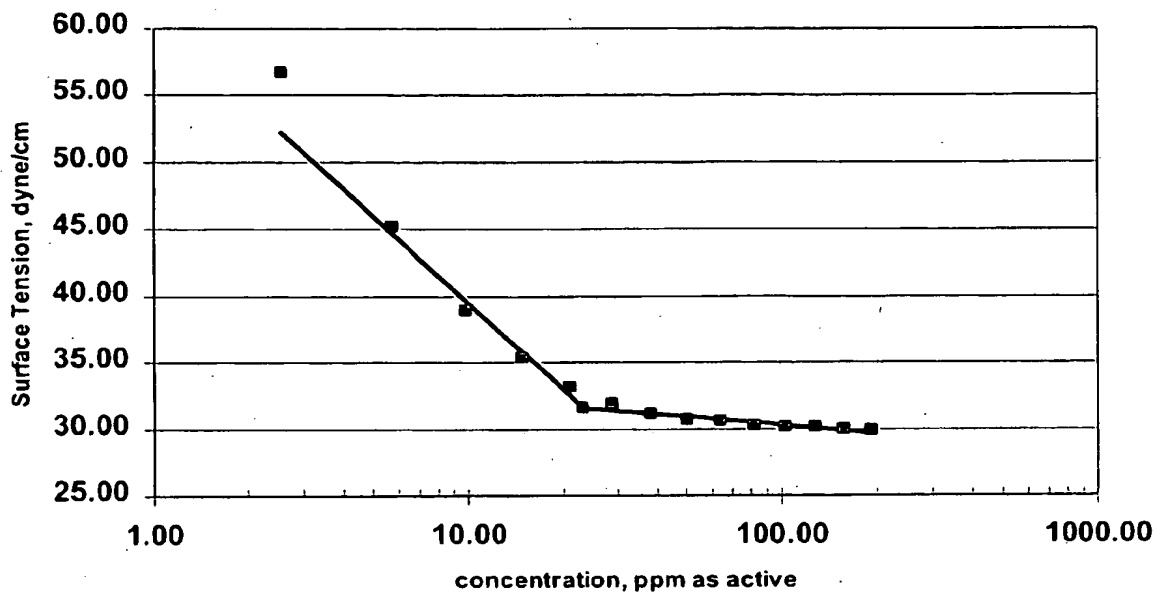


FIGURE 3

Surface Tension of Surfonamine ML-300 Amide/Acrylamide Copolymer
(50%:50% by weight) in Water



**Example 5 - preparation of ML-300 amide (example 1)/Methoxy
PEG of methacrylic acid copolymer (30/70 by weight)**

30 grams of Surfonamine® ML-300 amide, 70 grams of methoxy PEG methacrylic acid, and 100 grams of propylene glycol were combined in a flask and stirred under nitrogen. The mixture was heated to 115° C and 8 grams of solution containing tert-butyl perbenzoate and butanol at 1:1 ratio by weight was added slowly over 1 hour. The reaction was digested at 115°C for 2 hours, then stripped at 100°C for 1 hour under vacuum. The surface tension of this copolymer is shown in Fig. 4. The cmc is about 30 ppm and the minimum surface tension is about 30 dyne/cm.

Alkylamide MPEG Copolymer

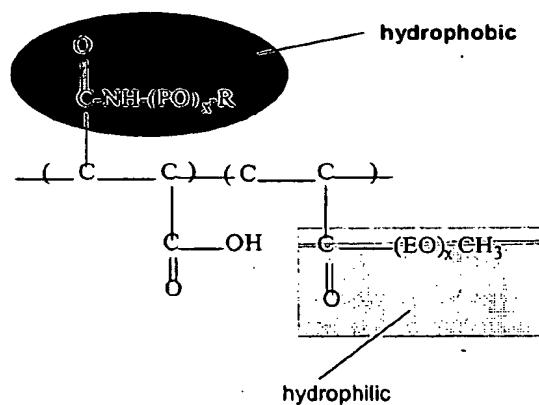
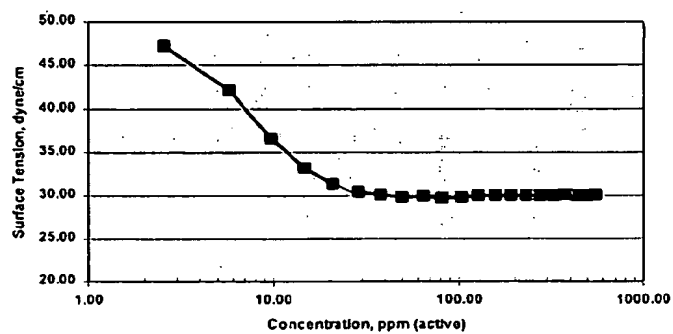


FIGURE 4
Surface Tension of Alkylamide
MethylPEG Copolymer in DI Water



What is claimed is:

- 1) A detergent composition providing enhanced cleaning performance comprising a surfactant, a surface active polymer, and water.
- 2) A detergent composition comprising a surfactant selected from the group consisting of: anionic surfactants, cationic surfactants, nonionic surfactants and zwitterionic surfactants, in combination with a surface active polymer set forth herein.
- 3) A composition useful as a prespotter comprising a composition according to claims 1 or 2.